

19



Europäisches Patentamt

European Patent Office

Office européen des brevets

11 Veröffentlichungsnummer:

11 Publication number:

11 Numéro de publication:

0 4 0 2 4 0 5

Internationale Anmeldung veröffentlicht durch die  
Weltorganisation für geistiges Eigentum unter der Nummer:

**WO 89/08138** (art.158 des EPÜ).

International application published by the World  
Intellectual Property Organisation under number:

**WO 89/08138** (art.158 of the EPC).

Demande internationale publiée par l'Organisation  
Mondiale de la Propriété Intellectuelle sous le numéro:

**WO 89/08138** (art.158 de la CBE).



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 4 :</b> <b>C10J 3/00, C01B 3/26</b>		<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 89/08138</b> <b>(43) International Publication Date:</b> 8 September 1989 (08.09.89)
<b>(21) International Application Number:</b> PCT/DK89/00048 <b>(22) International Filing Date:</b> 2 March 1989 (02.03.89)		<b>Published</b> <i>With international search report.</i>	
<b>(31) Priority Application Number:</b> P 38 06 732.2 <b>(32) Priority Date:</b> 2 March 1988 (02.03.88) <b>(33) Priority Country:</b> DE			
<b>(71)(72) Applicant and Inventor:</b> ANDERSEN, Kjeld [DK/DE]; Am Moor 9, D-2211 Mehlbek (DE).			
<b>(74) Agent:</b> LEHMANN & REE; Frederiksberg Allé 26, DK-1820 Frederiksberg C (DK).			
<b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.			
<b>(54) Title:</b> GASIFICATION PROCESS			
<b>(57) Abstract</b>  A catalytic process for converting an organic material into a gas by heating the organic material in liquid water to a temperature of from 200 to 450°C at a pressure of from 50 to 350 atmospheres in the presence of a catalyst comprising a compound of an element of group IA of the Periodic Table and a compound of an element of group IVB of the Periodic Table.			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT Austria	FR France	ML Mali
AU Australia	GA Gabon	MR Mauritania
BB Barbados	GB United Kingdom	MW Malawi
BE Belgium	HU Hungary	NL Netherlands
BG Bulgaria	IT Italy	NO Norway
BJ Benin	JP Japan	RO Romania
BR Brazil	KP Democratic People's Republic of Korea	SD Sudan
CF Central African Republic	KR Republic of Korea	SE Sweden
CG Congo	LI Liechtenstein	SN Senegal
CH Switzerland	LK Sri Lanka	SU Soviet Union
CM Cameroon	LU Luxembourg	TD Chad
DE Germany, Federal Republic of	MC Monaco	TG Togo
DK Denmark	MG Madagascar	US United States of America
FI Finland		

Gasification Process

This invention relates to a catalytic process for converting an organic material into a gas by heating the organic material in 5 liquid water to a temperature of from 200 to 450°C at a pressure of from 50 to 350 atmospheres in the presence of a catalyst comprising a compound of an element of group IA of the Periodic Table of Elements.

10 US patent specification No. 4.113.446 discloses a process of preparing a gas composition having a high heating value which process comprises reacting a liquid or solid organic material with water at a temperature of at least 647°K and at a pressure of at least 218 atmospheres to achieve the critical density of water. The 15 reaction is preferably carried out in the presence of a catalyst such as a hydrogenation catalyst.

Since the reaction is conducted at the critical density of water salts present in the material to be gasified will not be removed 20 together with the effluent and will consequently accumulate in the reactor used so that the operation has to be stopped at intervals to remove accumulated salts.

25 The published German patent application No. 37 05 781 discloses a process of the above-mentioned type. The composition of the gas produced by the prior art process depends on the composition of the starting material and the specific operational conditions used, but ordinarily the gas produced contains a mixture of carbon dioxide, carbon monoxide and methane and other low molecular weight 30 hydrocarbons. In such a liquid phase reaction salts can be removed from the reactor together with the liquid effluent so that an accumulation of the salts can be avoided.

35 The gas is suitable for use as a synthesis gas, e.g. a gas for the synthesis of methanol or hydrocarbons.

The prior art process suffers from the drawback that the product gas may contain char, coke, tar and/or oils which tend to be deposited on the catalyst and on the walls of the reaction chamber.

The invention is based on the discovery that organic materials can be gasified with little or no formation of char, coke and/or tar by heating the organic material in water in the presence of a catalyst which further comprises a compound of an element of group IVB of the  
5 Periodic Table of Elements.

In a particularly preferred embodiment of the process of the invention the group IVB compound is  $ZrO_2$ , which is stable under the severe temperatures used and which consequently can be reused.  
10

The reaction is preferably carried out at a temperature of from 270 to 380°C and at a pressure of from 150 to 270 atmospheres.

15 The organic material is preferably intimately mixed with the water. When employing a solid organic material such as coal or waste materials it is preferred that the solid is in the form of small particles and that the reaction is conducted so that the organic particles and water are formed and maintained as a slurry.

20 Any organic solid material can be employed herein such as garbage, paper, sawdust, dried sludge and other waste materials, cellulose waxes, coal, shale and the like. Also liquid organic materials such as sugars can be employed.

25 The weight ratio of organic material to water should be maintained at such a level that there is sufficient hydrogen available from the water to promote reforming and to prevent the formation of char or coke.

30 Generally the organic material will comprise from about 1 to about 50 percent by weight of the water.

35 The catalyst is preferably used in an amount of from about 5 to about 30 % by weight based on the weight of the organic material. The ratio of group IA compound to IVB compound is preferably in the range of 0.01:1 to 0.5:1.

The process can be carried out as either a batch process or as a continuous process.

In a continuous process a reaction slurry or a liquid mixture of the two reactants is fed to the reactor under heat and pressure and the product gas is drawn off continuously under high pressure thus eliminating the need of pressurizing the product gas in case it is 5 to be used in a high pressure process.

The reaction may be carried out in a vertical cylindrical reactor having an inlet for the introduction of starting material and water at the bottom of the reactor, an outlet for the gas formed at the 10 top of the reactor and an outlet for water provided in the upper part of the reactor.

The water removed through the latter outlet is preferably recycled and mixed with the incoming organic material.

15 It is advantageous to preheat the organic material, e.g. to a temperature of about 100°C, before it is mixed with the recycled water.

20 The process of the invention is also suitable for converting poisonous organic material such as halogenated hydrocarbons into non-poisonous compounds.

25 The invention will now be described in further detail with reference to the following examples.

Example 1

30 100 g barley straw were mixed with 900 ml ZrO<sub>2</sub> (in the form of tablets with a diameter of 3 mm and a surface area of 50 m<sup>2</sup>/g) and the mixture was introduced into a tubular reactor having a volume of 2 l. Subsequently 500 ml water and 10 g K<sub>2</sub>CO<sub>3</sub> were introduced therein.

35 The reactor was then closed and heated to a temperature of 360°C at a pressure of 220 atmospheres for 5 minutes. The conversion of the 100 g barley straw resulted in a gas having the following composition:

	CO <sub>2</sub>	59.9 % (w/w)
	H <sub>2</sub>	0.2 % (w/w)
	C <sub>1</sub> -C <sub>4</sub> hydrocarbons	2.8 % (w/w)
	Methanol	21.0 % (w/w)
5	Ethanol	6.8 % (w/w)
	Acetone	4.0 % (w/w)
	Propanol	3.0 % (w/w)
	Butanol	<u>2.0</u> % (w/w)
10	Total	100.3 % (w/w)

The reactor contained no tar, oil, coke or other solid decomposition products.

15 Example 2

320 g sewage corresponding to 100 g dry sludge were mixed with 900 ml of the same catalyst as described in example 1 and 12 g K<sub>2</sub>CO<sub>3</sub> in 380 g H<sub>2</sub>O and the mixture was transferred to the above-mentioned 20 reactor and tested under the same conditions as mentioned in example 1. 100 g dried sludge gave the following yields: CO<sub>2</sub> = 29.0 g, CO = 0.05 g, H<sub>2</sub> = 0.1 g, C<sub>1</sub>-C<sub>4</sub>-hydrocarbons = 1.1 g. Less than 1 % alcohols was formed, and approximately 23 g of other organic 25 compounds were found in the condensate. No coke, char or tar was deposited on the catalyst or on the reactor wall.

Example 3

This test was performed to show that this invention also may be 30 applied for converting poisonous organic compounds in waste water into gasses and other non-poisonous organic compounds. The test was performed in a tubular reactor with a volume of 680 ml. 2.2 l of an aqueous solution containing the following compounds:

35	Trichlorethane	0.14 % (w/w)
	Nitrobenzene	0.13 % (w/w)
	Chlorphenol	0.14 % (w/w)

and 2.0 % (w/w) of  $K_2CO_3$  were introduced into the reactor used in example 3 and was heated to a temperature of 360°C at a pressure of 225 atmospheres in the presence of 650 ml of  $ZrO_2$  with a surface area of 4  $m^2/g$  and a particle size of from 2-5 mm. The test gave the 5 following conversion data.

10 Trichlorethan 100 % conversion  
Nitrobenzene 100 % conversion  
Chlorphenol 83 % conversion

10

Comparison example

15 100 g barley straw and 630 ml of water containing 12.6 g  $K_2CO_3$  were placed in the reactor described in example 1. The test was then performed as described in example 1 and the following yields were obtained.  $CO_2$  = 24 g,  $CO$  = 0.3 g,  $H_2$  = 0.6 g,  $C_1-C_4$ -hydrocarbons = 4.6 g. 14 g of other organic compounds were found in the condensate. By opening the reactor it was found that the whole reactor wall was covered with coke. The deposited coke corresponded to 5.2 g carbon 20 or 12 % of the total carbon in the feed.

25

30

35

CLAIMS

1. A catalytic process for converting an organic material into a gas by heating the organic material in liquid water to a temperature of from 200 to 450°C at a pressure of from 50 to 350 atmospheres in the presence of a catalyst comprising a compound of an element of group IA of the Periodic Table of Elements characterized in that the catalyst further comprises a compound of an element of group IVB of the Periodic Table of Elements.  
10
2. A process according to claim 1, characterized in that the group IV compound is zirconiumdioxide.
3. A process according to claim 1 or 2, characterized in that the reaction is carried out at a temperature of from 270 to 15 380°C.
4. A process according to claim 1-3, characterized in that the reaction is carried out at a pressure of from 150 to 270 20 atmospheres.
5. A process according to any of the proceeding claims, characterized in that the organic material comprises from about 1 to about 50 % by weight of the water.  
25
6. A process according to any of the proceeding claims, characterized in that the catalyst is used in an amount of from about 5 to about 30 % by weight of the organic material.
7. A process according to any of the proceeding claims, characterized in that the ratio of group IA compound to group 30 IVB compound is in the range of 0.01:1 to 0.5:1.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/DK89/00048

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC 4

C 10 J 3/00, C 01 B 3/26

## II. FIELDS SEARCHED

Minimum Documentation Searched ?

Classification System	Classification Symbols
IPC 4	C 01 B; C 10 B; C 10 J
US C1	<u>48</u>

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

SE, NO, DK, FI classes as above

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	US, A, 4 113 446. (MICHAEL MODELL ET AL) 12 September 1978	
P,A	DE, A1, 3 705 781 (KJELD ANDERSEN) 1 September 1988	

\* Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

1989-06-02

Date of Mailing of this International Search Report

1989-06-14

International Searching Authority

Swedish Patent Office

Signature of Authorized Officer

Jan Carlerud